Airborne laser-induced oceanic chlorophyll fluorescence: solar-induced quenching corrections by use of concurrent downwelling irradiance measurements

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Airborne laser-induced (and water Raman-normalized) spectral fluorescence emissions from oceanic chlorophyll were obtained during variable downwelling irradiance conditions induced by diurnal variability and patchy clouds. Chlorophyll fluorescence profiles along geographically repeated inbound and outbound flight track lines, separated in time by ~3–6 h and subject to overlying cloud movement, were found to be identical after corrections made with concurrent downwelling irradiance measurements. The corrections were accomplished by a mathematical model containing an exponential of the ratio of the instantaneous-to-average downwelling irradiance. Concurrent laser-induced phycoerythrin fluorescence and chromophoric dissolved organic matter fluorescence were found to be invariant to downwelling irradiance and thus, along with sea-surface temperature, established the near constancy of the oceanic surface layer during the experiment and validated the need for chlorophyll fluorescence quenching corrections over wide areas of the ocean.

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1. Introduction

Airborne laser fluorosensors are frequently utilized in oceanographic field experiments to extend ship-determined chlorophyll measurements over wide areas.[1–6] Generally, airborne laser-induced and water Raman-normalized fluorescence determinations of chlorophyll have been found to be in good agreement with ship chlorophyll observations.[1,3,4] Most of this comparative data was acquired over relatively short time intervals near midday under clear or uniformly overcast conditions. Thus the laser-induced chlorophyll fluorescence observations were able to be empirically adjusted to the ship surface layer extraction without need for irradiance corrections. (The airborne laser-induced fluorescence observations are obtained from a low altitude of ~150 m, which is generally beneath any cloud cover.) It was necessary to fly under clear or uniformly cloudy sky conditions since there were at that time no supporting solar irradiance observations. The recent addition of a zenith-viewing cosine-collector–spectroradiometer to the airborne equipment complement now enables corrections for irradiance variability that is due to cloud conditions or changes in solar elevation.

The flights described herein were conducted under patchy clouds and were of long duration. Under these illumination conditions, the incident irradiance is a combination of (1) nearly constant diurnal variability and (2) high-spatial-frequency cloud-induced variability. For such compounded variability, downwelling irradiance measurements are required concurrently with the laser fluorescence measurements to effect a correction. We describe a mathematical correction to laser-induced chlorophyll fluorescence that utilizes concurrent downwelling irradiance measurements.

Chlorophyll fluorescence variations that are due to changes in the downwelling light field have been reported.[7] Thus it is well known that chlorophyll fluorescence displays significant short-term variability in response to changes in irradiance. This variability is a result of biological responses of photosynthetic apparatus to varying light regimes.[8] There are three factors that affect the fluorescence yield: (1) changes in photochemical conversion efficiency owing to saturation of the electron transport rates at suboptimal irradiance; (2) changes in nonphotochemical quenching within photosystem II reaction centers owing to photoinhibitory damage; (3) changes in the

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nonphotochemical quenching within photosystem II antennae owing to increased thermal deactivation of the absorbed energy. This third phenonenom (reversible solar-induced quenching of fluorescence) is mostly a consequence of rapidly reversible changes in the effective absorption cross section of the fluorescent target. In the case of chlorophyll *in vivo*, that target is photosystem II. The reversal process is induced when specific quenchers (xanthophylls) transfer the energy of the excitons to heat. The process is competitive with photochemistry and fluorescence and is a nonlinear function of incident solar radiation.[9] This phenomenon affects laser-induced fluorescence emissions and is the most common factor affecting the fluorescence yield. The patterns of fluorescence change in response to the varying irradiance reported herein most likely reflect this phenomenon. Chlorophyll fluorescence emission correction models to account for incident light field changes have also been given.[10,11] Our correction model uses a mathematical formulation similar to the one described in Ref. 10 and 11.

2. Materials and Methods

A. Airborne Instrumentation

The primary instrument used in this study was the NASA Airborne Oceanographic Lidar (AOL). The AOL and its ancillary equipment were flown on a four-engine NASA Goddard Space Flight Center P-3B aircraft at an altitude of ~150 m. Both the AOL and the P-3B aircraft are based at the Goddard Space Flight Center Wallops Flight Facility located on the Virginia coast. The AOL and its ancillary instrumentation have been discussed in numerous papers over the past 17 years.[2,12–15] The laser-induced fluorescence of the oceanic constituents and water Raman backscatter from the ocean surface layer were captured with a telespectroradiometer containing 32 contiguous ~11.25-nm-wide channels adjusted to span a 360-nm interval between 350 and 710 nm. The fluorosensor spectroradiometer is designed to permit the simultaneous acquisition of passive (solar-induced) upwelled oceanic radiance from these same channels through an electronically separate passive ocean color subsystem.[14,15] The passive ocean color subsystem is used to calibrate the AOL spectroradiometer radiometrically with a 0.75-m internally illuminated calibration sphere[16] and to verify the wavelength setting with sodium and mercury–cadmium spectral line sources.

The AOL laser transmitters consisted of two Nd:YAG lasers fired in alternating-pulses. The harmonic separator of one laser was set for frequency doubling (532-nm, ~300-mJ output) for phytoplankton excitation. (The 532-nm excitation wavelength yields chlorophyll fluorescence at 683 nm, water Raman emission at ~650 nm, and phycoerythrin fluorescence at ~570 nm.) The harmonic separator of the other laser was set for frequency tripling (355-nm, ~150-mJ output) for chromophoric dissolved organic matter (CDOM) excitation. (The 355-nm laser-induced backscatter spectra contain the broad organic fluorescence from ~380 to 600 nm, the water Raman backscattered spectral line centered at ~402 nm, and the phytoplankton chlorophyll fluorescence spectral band at ~683 nm.[15]) Consistent with the design specification of each of the Nd:YAG lasers, the 532-nm frequency-doubled laser was operated at 20 pulses/s whereas the 355-nm frequency-tripled laser was operated at 10 pulses/s. The airborne instrument complement also included a calibrated infrared radiometer (Barnes PRT-5) to provide sea-surface temperature (SST) measurements and a zenith-viewing single-channel radiometer subsystem equipped with a cosine collector to obtain downwelling irradiance.

B. Data Processing

The laser-induced spectra were subjected to a simple 1-s average to reduce both the volume of data and the sample-to-sample variability in the laser-induced fluorescence measurements. At the nominal 120-m/s velocity of the P-3B aircraft, each data point represents the mean value within the upper several meters of the vertical water column over a horizontal distance of approximately 120 m.

The laser-induced chlorophyll, phycoerythrin, and CDOM fluorescence were normalized by their respective concurrent water Raman backscattered signals. The water Raman normalization technique is a generally accepted procedure to remove the horizontal spatial variation in the optical properties of the upper water column.[17] The CDOM fluorescence present in the 402-nm water Raman channel from the 355-nm excitation was removed using a ratio of 0.6 of the CDOM fluorescence found in the 450-nm channel. The 0.6 factor in the relationship in CDOM fluorescence between 402 and 450 nm was developed from the laboratory analysis of 178 samples acquired during ship surveys conducted in the Middle Atlantic Bight, Monterey Bay, and the Gulf of Mexico.[4,6,18]

C. Airborne Field Experiment

On 28 October 1993 a flight experiment was conducted from 1600 to 1730 Greenwich Mean Time on a 950-km outbound track line between 2 °S/81 °W and ~5 °S/91 °W. A comparable flight line was occupied again in the reverse direction from 2030 to 2200 Greenwich Mean Time. On both flight lines, the bases of the low-lying cumulus–nimbus clouds were present above the 150-m flight altitude of the aircraft. The flight lines (Fig. 1) were executed in transit to and return from the 1993 Iron Enrichment Experiment[19–21] site located in blue waters of the eastern equatorial Pacific Ocean west of Ecuador.

3. Results

The chlorophyll, phycoerythrin, chromophoric dissolved organic matter fluorescence, and SST profiles obtained during repeated outbound and inbound transits to and from the Iron Enrichment Experiment are shown in Fig. 2. The chlorophyll fluorescence profiles [Fig. 2(a)] exhibit poor agreement and show considerable differences over most of the flight line.

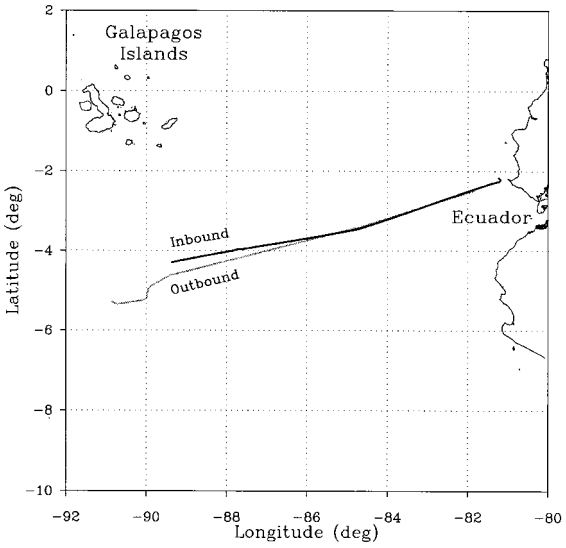

Fig. 1. Location of the outbound and inbound airborne flight lines from Ecuador. The flight was conducted at 150 m altitude, and the aircraft was at all times beneath the bases of the low-lying cumulus–nimbus clouds. The flight lines were not geographically repeated over their entire length and can be seen to depart considerably (~25 km) toward the western end.

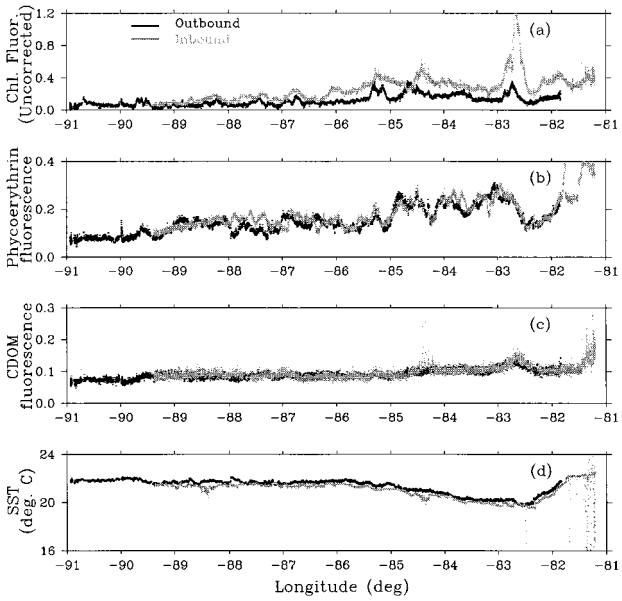

Fig. 2. Corresponding outbound and inbound flight track profiles uncorrected for downwelling irradiance. (a) Inbound laser-induced and water Raman-normalized chlorophyll fluorescence profile exhibits a significant increase as the incident irradiance [see Fig. 3(a)] declines. Sizeable disagreement is found where, after ~6 h, the irradiance is lowest, e.g., at −82°. (b) Phycoerythrin fluorescence, (c) CDOM fluorescence, and (d) SST show good agreement over the 3–6 h. period separating the observations. The latter three profiles indicate that the oceanographic conditions of the surface layer were essentially unchanged from 1600 to 2200 Greenwich Mean Time and that these parameters were essentially unaffected by downwelling irradiance changes.

In contrast the phycoerythrin fluorescence, CDOM fluorescence, and SST [Figs. 2(b), 2(c), and 2(d)] show quite good agreement although 3–6 h had elapsed between the outbound and the inbound measurements. The temporal invariance of phycoerythrin fluorescence, CDOM fluorescence, and SST indicates that the oceanographic conditions of the surface layer were essentially unchanged during that time period.

Figure 3(a) shows the downwelling irradiance measured by a zenith-viewing wide-bandwidth visible radiometer. The irradiance profiles exhibit slow diurnal changes (resulting from the 3–6-h sampling separation) modulated with high-frequency cloud-induced variations. For example, at ~−89° longitude the general level of the downwelling irradiance for the inbound flight track is only slightly lower than for the outbound track, whereas considerable differences can be seen near −82° longitude, where the temporal separation was greatest. The high-frequency variations are caused by clouds. Blue-sky regions display relatively flat signatures having only diurnal variation. Examples of such regions can be seen at ~−82.7° and ~87.9° on the outbound leg and at ~−83.1° − 83.7° on the inbound leg. Note that immediately on either side of a blue sky region the measured irradiance is elevated by direct reflection from the sides of the adjacent clouds. The downwelling irradiance in Fig. 3(a) was used to correct the chlorophyll fluorescence on both the outbound and inbound track lines. [The irradiance in Fig. 3(a) is measured at the aircraft, but the value at the ocean surface 150 m below is the same within experimental error.] The correction has the following form:

$$F_{\text{corrected}} = F_{\text{uncorrected}}[1 + \exp(E_d/E_{d,\text{avg}} - 1)], \quad (1)$$

where F is the water Raman-normalized chlorophyll fluorescence, E_d is the downwelling irradiance, and $E_{d,\text{avg}}$ is the mean downwelling irradiance over the ~6-h period encompassing the airborne measurements. Note that the downwelling irradiance sen-

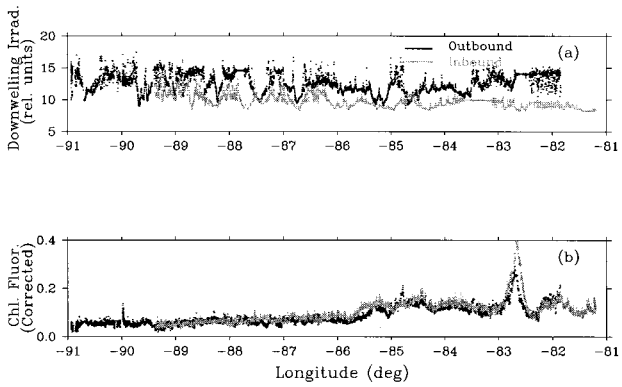

Fig. 3. (a) Corresponding inbound and outbound flight track profiles of downwelling irradiance from zenith-viewing wide-bandwidth visible radiometer. On both outbound and inbound track lines, irradiance exhibits gradual diurnal changes modulated with high-frequency cloud-induced variations. The inbound track line was traversed from 2030 to 2200 and declines toward shore. (b) Airborne laser-induced and water Raman-normalized chlorophyll fluorescence show excellent agreement after correction for downwelling irradiance [compare with the uncorrected fluorescence Fig. 2(a)].

sor need not be calibrated to provide the required data. However, the irradiance sensor must be linear over the entire amplitude range of the measurements.

The results of the corrections are shown in Fig. 3(b). The chlorophyll fluorescence profiles are in excellent agreement when corrections are made for downwelling irradiance. The region of most disagreement is the chlorophyll patch at approximately −82.7°. This disagreement may be due to oceanographic variability during the elapsed time of ~5.5 h. This is substantiated by the equivalent chlorophyll fluorescence levels on either side (−82° and −83°) of the event.

4. Discussion

Solar-induced quenching of phytoplankton chlorophyll fluorescence is an experimentally documented phenomenon,[8] and some photosystem modeling efforts have successfully addressed the effect. In particular, chlorophyll fluorescence changes that are due to downwelling light field variability have been reported.[1] Photosystem modeling has provided insight and mathematical equations to correct chlorophyll fluorescence resulting from variability in the downwelling light field.[10,11] We have shown that corrections applied with a model formulation similar to that of Guenther[10,11] successfully removed variability in the laser-induced fluorescence that we observed in the eastern equatorial Pacific Ocean. While other irradiance–fluorescence experiments[1,10,11] have been limited to specific locations, the airborne experiment here confirms that such effects are widespread and that corrections are required over expansive regions of the ocean.

We believe it would be of interest to investigate quenching in other water bodies. Although quenching has been observed in airborne chlorophyll fluorescence on the continental shelf of the Middle Atlantic Bight, our unpublished data for the Middle Atlantic Bight suggest that the depth or intensity of the quenching, for unknown reasons, is small even for downwelling irradiance variation comparable with that encountered in the eastern equatorial Pacific Ocean. Specific field experiments are recommended to establish the dominant mechanisms responsible for this quenching variability.

The concurrent phycoerythrin fluorescence showed no obvious quenching effects. Perhaps the airborne field data were not taken at sufficiently depressed downwelling irradiance levels to observe laser-induced phycoerythrin fluorescence quenching, or differences in photosystem fluorescence kinetics exist between chlorophyll and phycoerythrin. The eastern equatorial Pacific Ocean data herein suggest that phycoerythrin fluorescence is not highly variable in partly cloudy, daytime ambient irradiance levels under which most airborne field experiments would be conducted. Our field results suggest that phycoerythrin fluorescence measurements need no correction over a considerable range of downwelling irradiance.

In addition to biomass estimation, the quenching correction methods herein may enhance future laser system development of airborne fast repetition rate or pump-and-probe techniques.

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